Ultrasonic Solution Degradations of Polystyrene and Substituted Polystyrenes in Tetrahydrofuran as Solvent

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ABSTRACT

Ultrasonic (70 W, 20 kHz) solution (2% THF) degradations of polystyrene (PS), poly(α-methylstyrene) (PαMeS), poly(p-isopropyl α-methylstyrene) (PpiPrαMeS), poly(p-chlorostyrene) (PpClS), poly(p-bromostyrene) (PpBrS), and poly(p-methoxystyrene) (PpOMeS) have been carried out in tetrahydrofuran at 27°C. The average number of chain scissions S (where S = $[(\overline{M}_n)_0/(\overline{M}_n)_t]$ - 1), computed from the overall values of $(\overline{M}_n)_0$ and $\overline{M}_n)_t$, were found to be different from those of S' (where S' = $\alpha([\overline{M}_n)_0/(\overline{M}_n)_t]$ - 1)) based on the component (only that part of the polymer which is involved in degradation) data of the weight fraction (α), $(\overline{M}_n)_0$, and $(\overline{M}_n)_t$. S' for polystyrene and substituted polystyrene follows the order PS > PpClS > PpiPrαMeS > PpBrS > PpOMeS > PαMeS. In the case of PS where degradations were also carried out at -20°C, lowering of the temperature increased the weight fraction of polymer degraded as well as S. Based on the viscosity and GPC data, it is concluded that the ultrasonic solution degradation of PS does not lead to branched polymers.

INTRODUCTION

Ultrasonic solution degradations of polystyrene [1] and poly(α-methylstyrene) [2] are well documented. When polymer solutions are subjected to ultrasonic treatments, shearing of polymer molecules yields homolytic cleavage [3-7] due to cavitation [8-14]. These degradations have been mostly carried out in dilute solutions as cavitation is difficult to achieve in viscous media. Other parameters which may also affect ultrasonic solution degradation of polymers are pressure [15, 16], temperature [10-17], frequency [18] and intensity [10, 19-27] of ultrasound, reactor design [28-30], and molecular weights of the starting materials [17-25]. In the present studies, ultrasonic solution degradations of polystyrene (PS), poly(α-methylstyrene) (PαMeS), poly(p-isopropyl α-methylstyrene) (PpiPrαMeS), poly(p-bromostyrene) (PpBrS), poly(p-chlorostyrene) (PpClS), and poly(p-methoxystyrene) (PpOMeS) have been carried out at constant conditions of pressure (atmospheric), frequency (20 kHz), intensity (70 W), and concentration (2% in THF) as a function of time. The principal results of these studies are reported here.

EXPERIMENTAL

Materials

Polystyrene (Pressure Chemical Co.); poly(p-chlorostyrene), poly(p-bromostyrene), and poly(p-methoxystyrene), (Aldrich Chemical Co.); and poly(α-methylstyrene) [31] and poly(p-isopropyl α-methylstyrene) [32] were used in the present study.

Degradation Procedure

Ultrasonic degradations of polymer solutions in THF were carried out in a batch reactor (10 cm long, 2.5 cm diameter, 50 mL capacity), equipped with a water jacket to maintain a 2°C temperature within, measured with a Ni-Cr alloy probe and a Comark digital thermometer [17, 33]. The sealed steel reactor was screwed onto a threaded nodal point on a 1.25 cm diameter disruptor horn (Heat systems, Model 375 A with a nominal frequency of 20 kHz). The ultrasonic intensity of 70 W was adjusted using the calibration curve of the meter reading, the power control setting, and the power output in watts. After sonicating the polymer solutions for a desired period of time, these were transferred to 120 mL capped bottles for viscosity and gel permeation chromatographic analyses.

Characterization of Polymers

Viscosity

Calculation of the intrinsic viscosity of the original as well as of the sonicated polymers was carried out in THF at 25°C as well as in toluene at 30°C, making use of the flow time measurement data obtained with Ubbelohde viscometers for at least four concentrations. Knowing the flow time of the solvent and the solutions, the computation of the intrinsic viscosity $[\eta]$ is carried out with

$$[\eta] = \lim_{c \to 0} \eta_{sp}/c \tag{1}$$

where

$$\eta_{sp}/c = \left(\frac{\text{flow time of solution}}{\text{flow time of solvent}} - 1 \right)$$

Huggins coefficient k_H is related to $[\eta]$ by

$$(\eta_{sp}/c) = [\eta] + k_H[\eta]^2 c \tag{2}$$

By making use of Mark-Houwink constants K and a [34] for PpClS, PpBrS, and PpOMeS in toluene, molecular weights $\overline{M}_v$ were computed for these polymers. Combining these molecular weights with those obtained from GPC data, K and a for PpClS (1.34×10^{-3} dL/g, 0.54) PpBrS (3.18×10^{-5} dL/g, 0.77) and PpOMeS (2.2×10^{-5} dL/g, 0.79) were obtained at 25°C.

Gel Permeation Chromatographic Analyses

Molecular weight distributions of polymers were carried out with a Waters Associates GPC [equipped with a high pressure solvent delivery system, (Model 6000 A), ultraviolet absorbance detector (Model 440) and a differential refractometer (Model R-401)] operated at 25°C. The separating system consisted of four μ-Styragel columns connected in series, each packed with cross-linked polystyrene gel (by the Waters method) having pore sizes of 500, 1×10^3, 1×10^4, and 1×10^5 Å, respectively. The flow of solvent was maintained at 1 mL/min while the concentration of polymer solution was limited to 0.2% in order to render negligible the "concentration effects" on the peak position in the chromatograms. Calibration of the instrument was performed with PS standards as well as with other substituted polystyrenes of predetermined molecular weights. Calibration curve

relating elution volume V_e and molecular weight $\overline{M}$ for PS (Eq. 3) PpClS (Eq. 4), PpBrS (Eq. 5), PpOMeS (Eq. 6), PαMeS (Eq. 7), and PpiPrαMeS (Eq. 3) are as follows:

$$\ln \overline{M} = 24.03 - 0.440 V_e \tag{3}$$

$$\ln \overline{M} = 25.35 - 0.496 V_e \tag{4}$$

$$\ln \overline{M} = 22.20 - 0.365 V_e \tag{5}$$

$$\ln \overline{M} = 24.93 - 0.456 V_e \tag{6}$$

$$\ln \overline{M} = 24.93 - 0.428 V_e \tag{7}$$

With the help of Eqs. (3) to (7), $\overline{M}_w$ and $\overline{M}_n$ of the degraded homopolymers were computed from their uncorrected GPC chromatograms using the summation method [35].

RESULTS AND DISCUSSION

The solution properties of PS ($\overline{M}_w = 9.0 \times 10^5$, $\overline{M}_w/\overline{M}_n = 1.3$) before and after its ultrasonic degradation at 27 and -20°C for various periods of time are presented in Table 1. Molecular weights $\overline{M}_w$ (Fig. 1) and $\overline{M}_n$ computed from GPC chromatograms decrease with increasing irradiation time while the $\overline{M}_w/\overline{M}_n$ ratio remains constant within ±0.2 of 1.35 and do not approach a value of 2.0 which is typical of random-scission mechanism. This would suggest that even after 480 min of irradiation at 27°C and 240 min of irradiation at -20°C, the limiting chain-length below which no degradation takes place has been achieved. Huggins coefficients, k_H, of the degraded polymers stay within ±0.06 of 0.44. This value is characteristic of random coil. The average number of scissions S ($S = [(\overline{M}_n)_0/(\overline{M}_n)_t] - 1$) [36-40] for the ultrasonic solution degradation of PS ($\overline{M}_w = 9.0 \times 10^5$) decreases with increasing irradiation time. These calculations of S min^{-1} are based on the conventional method of using overall values of $(\overline{M}_n)_0$ and $(\overline{M}_n)_t$. However, as in ultrasonic solution degradations, only a part of the polymer is involved initially, so the use of overall molecular weights is questionable. In order to overcome this objection, an alternate approach of analyses was developed [41, 42] where

TABLE 1. Ultrasonic (70 W, 20 kHz) Solution (2% THF) Degradation of PS ($\overline{M}_w = 9.0 \times 10^5$) for Various Periods of Time

No.	Irradiation time (min)	Temperature (°C)	$\overline{M}_w \times 10^{-4}$ (GPC)	$\overline{M}_n \times 10^{-4}$ (GPC)	$\overline{M}_w/\overline{M}_n$	$[\eta]^a$ (dL/g)	Huggins coefficient k_H	S min^{-1} $\times 10^3$
-	Nonirradiated	-	90.0	70.0	1.3	2.25	-	-
X-104	7.5	27	66.0	52.0	1.25	-	-	46.0
X-105	15	27	61.0	48.0	1.25	-	-	30.0
X-106	30	27	62.5	47.0	1.33	1.92	-	16.0
X-107	60	27	53.0	37.5	1.40	1.74	0.38	14.4
X-108	120	27	48.0	33.5	1.43	1.51	0.41	9.1
X-109	180	27	42.0	29.0	1.43	1.34	0.45	7.8
X-110	270	27	27.5	19.0	1.44	0.93	0.43	9.9
X-111	360	27	30.0	20.0	1.50	0.81	0.40	6.9
X-112	480	27	26.0	18.0	1.45	-	0.50	6.0
X-274	30	-20	49.5	30.5	1.6	-	-	43.2
X-275	60	-20	51.0	35.0	1.45	-	-	16.7

(continued)

TABLE 1 (continued)

No.	Irradiation time (min)	Temperature (°C)	$\overline{M}_w \times 10^{-4}$ (GPC)	$\overline{M}_n \times 10^{-4}$ (GPC)	$\overline{M}_w/\overline{M}_n$	$[\eta]^a$ (dL/g)	Huggins coefficient k_H	S min^{-1} $\times 10^3$
X-276	120	-20	23.5	15.0	1.55	-	-	30.5
X-277	180	-20	20.0	13.5	1.47	-	-	23.2
X-278	240	-20	16.0	11.0	1.47	-	-	16.0

[a]In THF at 25°C, $\overline{M}_w$ and $\overline{M}_n$ values listed in this table are not absolute due to poor separation of high molecular weight polymers in GPC.
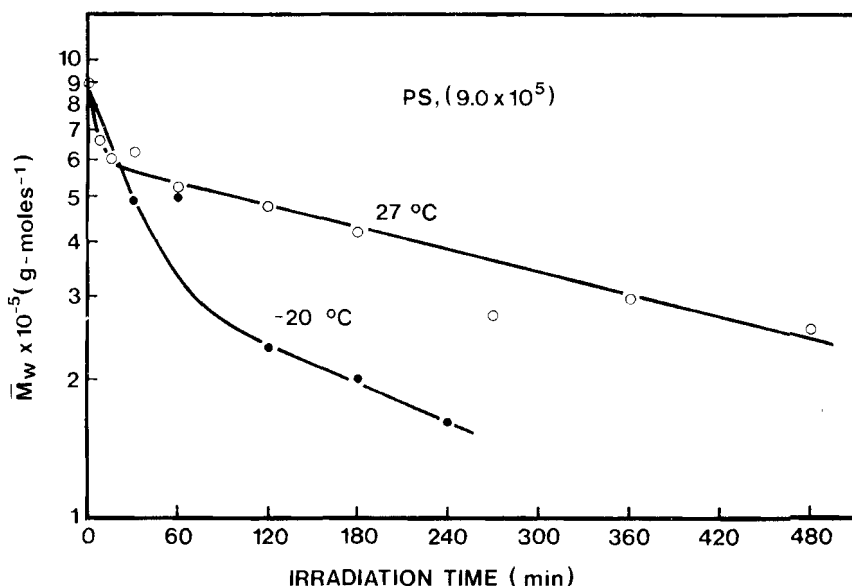
FIG. 1. Variation of molecular weights as a function of irradiation time for PS ($\overline{M}_w$ = 9.0 × 10^5): (○) 27°C and (●) -20°C. (See Table 1 for other data.)

the normalized GPC chromatograms (area under each chromatogram being unity of degraded polymers) were compared with that of the original polymer as shown in Fig. 2. One notes that in the first 120 min of ultrasonic degradation (Fig. 2a), an area marked with vertical hash lines (-) has disappeared from the original distribution and has reappeared elsewhere, possibly that marked with horizontal hash lines (+). On converting these areas into distributions (Fig. 2b), one can readily visualize the changes resulting from the decomposition of higher molecular weight species. Making use of $(\overline{M}_n)_0$ and $(\overline{M}_n)_t$ of these components in conjunction with their weight fraction (α), normalized values of S' are computed as follows: S' = $\alpha([(\overline{M}_n)_0 / (\overline{M}_n)_t] - 1)$.

Figure 3 shows component degradation of PS ($\overline{M}_w$ = 9.0 × 10^5) at 27 and -20°C for periods of 60, 120, and 180 min. Under identical conditions of ultrasonic solution treatment of PS, more polymer is involved in degradation at -20°C than at 27°C. S' min^{-1} values calculated using $(\overline{M}_n)_0$, $(\overline{M}_n)_t$, and α of these components are presented in Table 2. Values for the average number of scissions S min^{-1} (6.0-14.4) × 10^{-3} at 27°C and (16.0-43.2) × 10^{-3} from the overall
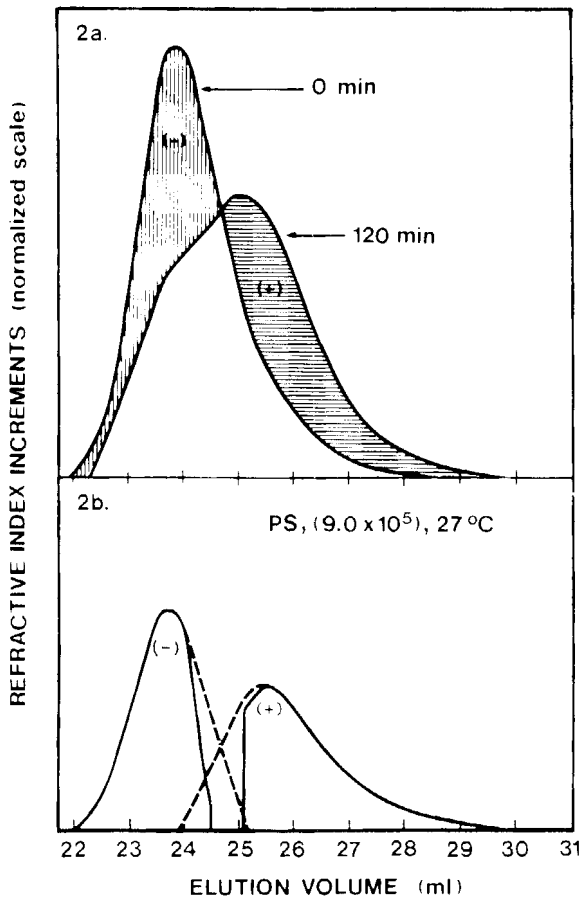
FIG. 2. Graphical method of analysis by which GPC distribution curves are broken down into their components: case of PS ($\overline{M}_w = 9.0 \times 10^5$) subjected to ultrasonic treatment at $27°C$ for a period of 120 min.
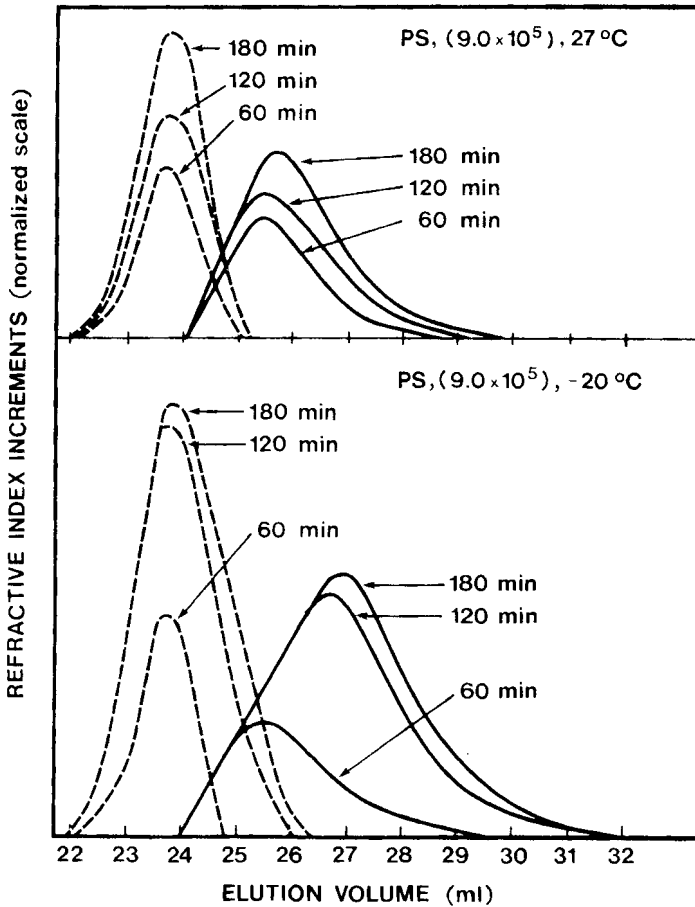
FIG. 3. Component degradation of PS ($\overline{M}_w$ = 9.0 × 10⁵) at 27 and -20°C for periods of 60, 120, and 180 min. (See Table 2 for other data.)

TABLE 2. Ultrasonic (70 W, 20 kHz) Solution (2% THF) Degradation of PS ($\overline{M}_w = 9.0 \times 10^5$)

No.	Irradiation time (min)	Temperature (°C)	Weight fraction (α)	Before degradation			After degradation			S' normalized values	S' min^{-1} ×10^3	S min^{-1} ×10^3
				$\overline{M}_w$ ×10^{-4}	$\overline{M}_n$ ×10^{-4}	$\dfrac{\overline{M}_w}{\overline{M}_n}$	$\overline{M}_w$ ×10^{-4}	$\overline{M}_n$ ×10^{-4}	$\dfrac{\overline{M}_w}{\overline{M}_n}$			
X-107	60	27	0.25	92.8	86.8	1.07	37.5	30.8	1.22	0.45	7.6	14.4
X-108	120	27	0.38	90.0	84.0	1.07	35.0	27.5	1.27	0.78	6.5	9.1
X-109	180	27	0.46	92.1	86.2	1.07	33.3	25.7	1.29	1.08	6.0	7.8
X-110	270	27	0.75	85.6	78.2	1.10	27.4	21.8	1.25	1.95	7.0	9.9
X-112	480	27	0.76	85.6	78.2	1.10	27.4	21.8	1.25	1.95	4.0	6.0
X-274	30	-20	0.32	88.4	83.9	1.05	34.8	26.9	1.29	0.67	22.0	43.2
X-276	120	-20	0.84	82.5	74.4	1.10	24.8	16.7	1.48	2.90	24.0	30.5
X-277	180	-20	0.95	79.0	70.0	1.13	22.7	15.6	1.45	3.33	18.0	23.2
X-278	240	-20	1.0	75.0	64.4	1.16	21.0	13.8	1.52	3.89	16.0	16.0

TABLE 3. Ultrasonic (70 W, 20 kHz) Solution (2% THF) Degradation of PαMeS ($\overline{M}_w$ = 2.0 × 10^5) at 27°C for Various Periods of Time

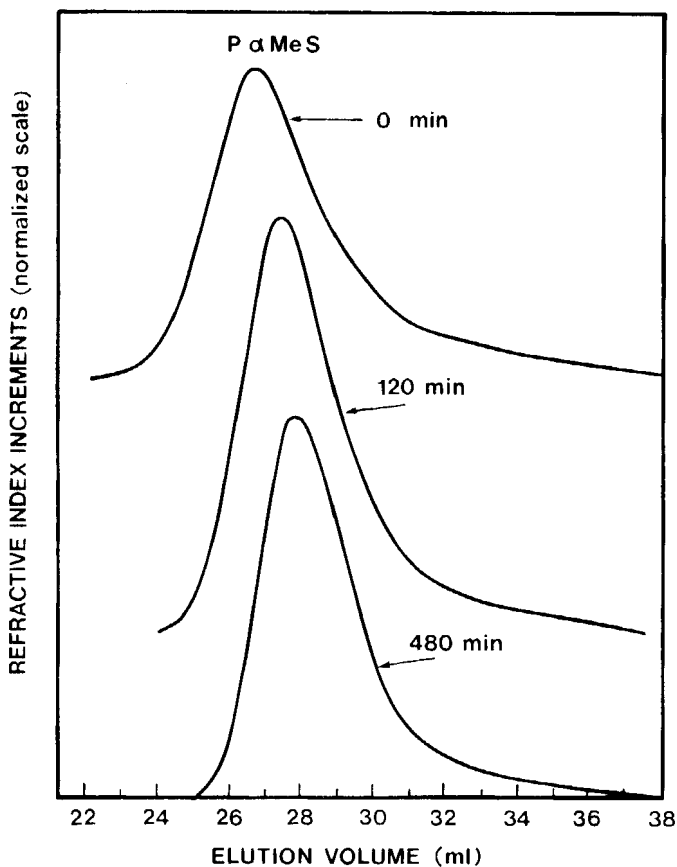| No.	Irradiation time (min)	$\overline{M}_w \times 10^{-3}$ (GPC)	$\overline{M}_n \times 10^{-3}$ (GPC)	$\overline{M}_w/\overline{M}_n$	[η] in THF at 25°C (dL/g)	k_H
-	Nonirradiated	200	58	3.37	-	-
X-136	60	170	57	3.0	0.47	0.38
X-135	120	140	56	2.55	-	-
X-134	180	115	50	2.3	0.38	0.20
X-133	270	105	47	2.2	0.33	0.32
X-132	360	100	47	2.1	0.31	0.41
X-131	480	100	47	2.1	-	-

FIG. 4. Normalized GPC chromatograms before and after ultra-
sonic solution degradation of PαMeS at 27°C for various periods of
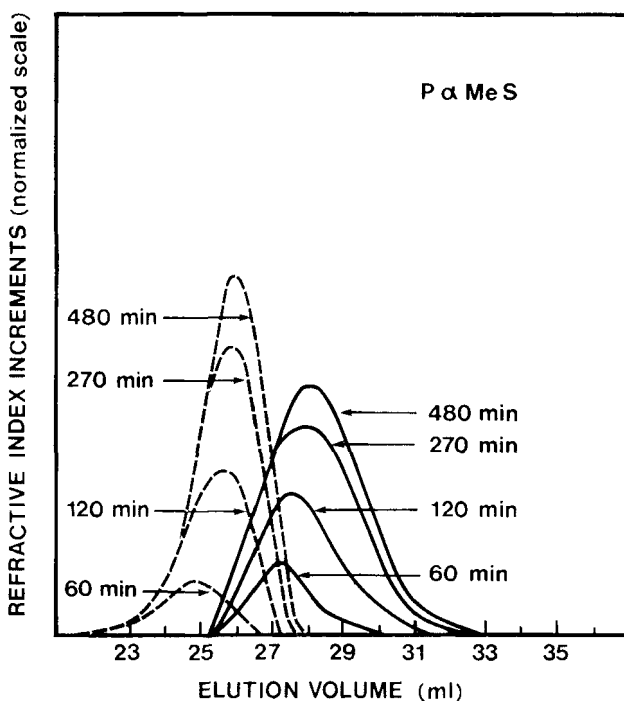time. (See Table 3 for other data.)

FIG. 5. Component degradation of PαMeS ($\overline{M}_w$ = 2.0 × 10^5) at 27°C for various periods of time. (See Table 4 for other data.)

molecular weights are higher than those (4.0-7.6) × 10^{-3} at 27°C and (16.0-22.0) × 10^{-3} at -20°C computed on the basis of component analyses. This suggests that data on S min^{-1} cited in the literature should be treated with caution.

In Table 3 are presented data on molecular weights, viscosity, and k_H for the ultrasonic solution degradation of PαMeS ($\overline{M}_w$ = 2.0 × 10^5) at 27°C. $\overline{M}_w$ decreases with increasing irradiation time; however, $\overline{M}_n$ values do not show significant decreases on irradiation. This does not permit to evaluate S min^{-1}. However, S' min^{-1}, computed from normalized GPC distribution (Fig. 4) comparisons leading to component tracing (Fig. 5) and their analyses (Table 4) for PαMeS (1.7-3.98) × 10^{-3} are significantly lower than those for PS. It is worthwhile mentioning that lower values of S' min^{-1} in the case of PαMeS as compared to those for PS may arise due to lower initial $\overline{M}_w$ of the former polymer. S' min^{-1} values ranging from (14.0-32.0)

TABLE 4. Ultrasonic (70 W, 20 kHz) Solution (2% THF) Degradation of PαMeS at 27°C

No.	Irradiation time (min)	Weight fraction (α)	Before degradation			After degradation			S' normalized values	S' min^{-1} $\times 10^3$
			$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\dfrac{\bar{M}_w}{\bar{M}_n}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\dfrac{\bar{M}_w}{\bar{M}_n}$		
X-107	60	0.06	52.9	46.4	1.16	16.7	14.4	1.33	0.14	2.33
X-108	120	0.21	39.4	33.8	1.16	13.7	11.0	1.25	0.44	3.70
X-109	180	0.36	35.0	30.2	1.16	13.9	10.1	1.38	0.72	3.98
X-110	270	0.36	35.0	30.1	1.16	9.5	7.8	1.22	1.03	3.81
X-111	360	0.40	33.3	28.4	1.17	10.1	7.5	1.34	1.11	3.09
X-112	480	0.43	32.7	28.1	1.16	12.9	9.7	1.33	0.82	1.70

TABLE 5. Ultrasonic (70 W, 20 kHz) Solution (2% THF) Degradation of PpiPraMeS ($\overline{M}_w$ = 2.0 × 10⁵) at 27°C for Various Periods of Time

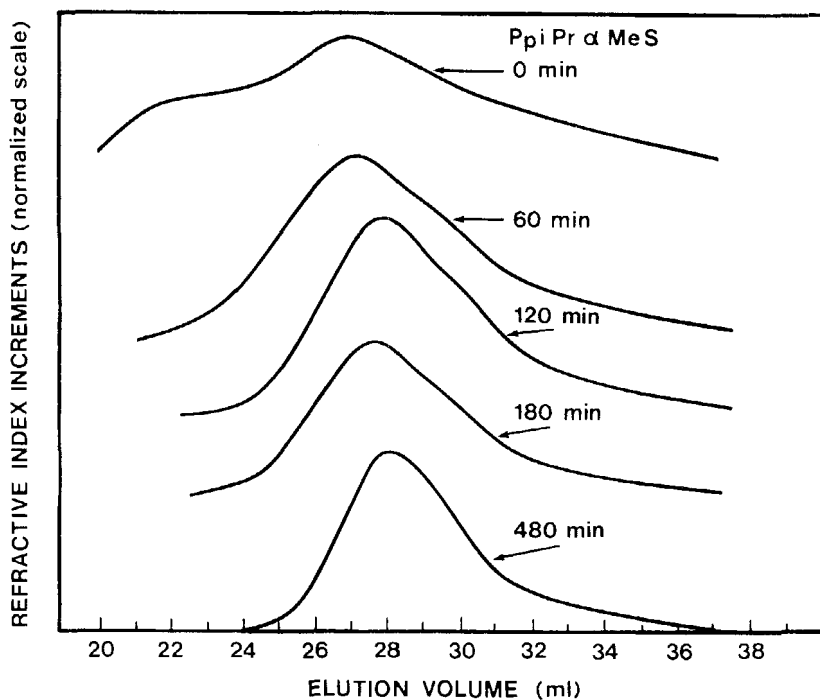| No.	Irradiation time (min)	$\overline{M}_w \times 10^{-3}$ (GPC)	$\overline{M}_n \times 10^{-3}$ (GPC)	$\overline{M}_w/\overline{M}_n$	[η] in THF at 25°C (dL/g)	k_H
-	Nonirradiated	200	33.0	6.0	-	-
X-142	60	180	33.0	5.5	0.34	0.53
X-141	120	130	29.0	4.4	0.32	0.30
X-140	180	150	33.0	4.5	0.30	0.31
X-139	250	110	34.0	3.3	-	-
X-138	330	120	36.5	3.3	0.27	0.14
X-137	480	105	37.5	2.85	-	-

FIG. 6. Normalized GPC chromatograms before and after ultra-sonic solution degradation of PpiPrαMeS ($\overline{M}_w$ = 2.0 × 10^5) at 27°C for various periods of time. (See Table 5 for other data.)

× 10^{-3} at 27°C and (53.0-116.0) × 10^{-3} at -20°C for PS ($\overline{M}_w$ = 1.8 × 10^6) [42] are higher than those for PS ($\overline{M}_w$ = 9.0 × 10^5) which varied from (6.0-14.4) × 10^{-3} at 27°C and (16.0-43.2) × 10^{-3} at -20°C.

In Table 5 are presented data on molecular weights, viscosity, and k_H for the ultrasonic solution degradation of PpiPrαMeS ($\overline{M}_w$ = 2.0 × 10^5) at 27°C. $\overline{M}_w$ decreases while $\overline{M}_n$ remains essentially constant on increasing the irradiation time. S' min^{-1} calculated from the normalized GPC distribution (Fig. 6) comparisons leading to component tracing (Fig. 7) and their analyses (Table 6) for PpiPrαMeS (3.8-30.2 × 10^{-3}) are far greater than those for PαMeS. This is also reflected in the decrease of overall $\overline{M}_w$ (Fig. 8) for the two polymers, viz., PαMeS and PpiPrαMeS, with identical initial $\overline{M}_w$ where the latter degrades faster than the former. One may be tempted
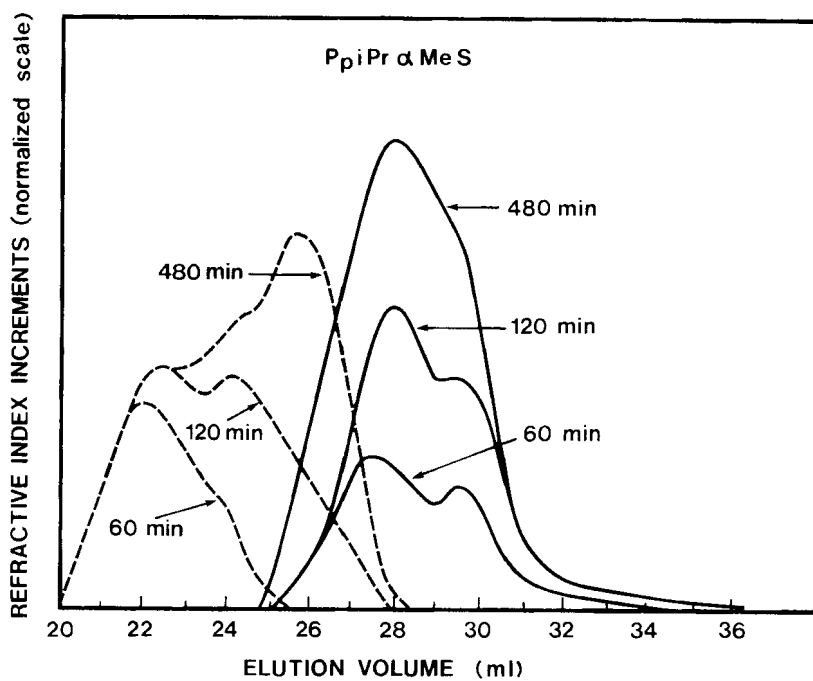
FIG. 7. Component degradation of PpiPrαMeS at 27°C for various periods of time. (See Table 6 for other data.)

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TABLE 6. Ultrasonic (70 W, 20 kHz) Solution (2% THF) Degradation of PpiPrαMeS ($\overline{M}_w$ = 2.0 × 10^5) at 27°C

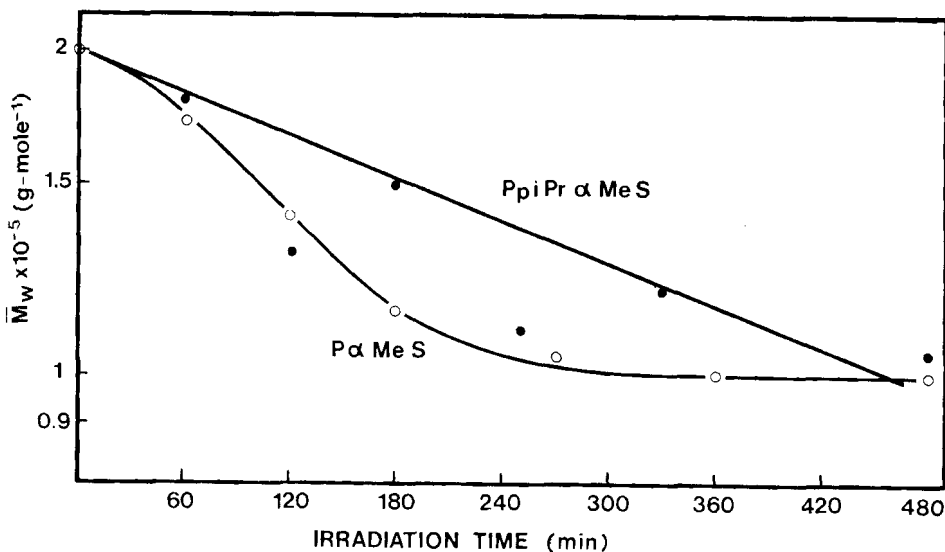| No.	Irradiation time (min)	Weight fraction (α)	Before degradation			After degradation			S' normalized values	S' min^{-1} × 10^3
			$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\dfrac{\overline{M}_w}{\overline{M}_n}$	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\dfrac{\overline{M}_w}{\overline{M}_n}$		
X-142	60	0.14	145.0	116.0	1.25	11.3	8.30	1.37	1.81	30.2
X-141	120	0.26	100.0	58.8	1.70	9.4	6.20	1.50	2.20	18.4
X-140	180	0.27	101.0	62.1	1.63	11.9	7.88	1.51	1.86	10.3
X-138	330	0.35	86.7	50.3	1.73	12.4	8.65	1.44	1.68	5.1
X-137	480	0.42	77.0	42.3	1.82	11.7	7.87	1.50	1.84	3.8

FIG. 8. Variation of molecular weights, $\overline{M}_w$, as a function of irradiation time for PαMeS and PpiPrαMeS at 27°C. (See Tables 3 and 5 for other data.)

to conclude that the para substituent isopropyl in PpiPrαMeS has something to do with it; however, it should be noted that there are more higher molecular weight species ($\overline{M}_w/\overline{M}_n = 6.0$) in PpiPrαMeS than in PαMeS ($\overline{M}_w/\overline{M}_n = 3.37$). In Fig. 8 are shown variations of overall $\overline{M}_w$ as a function of irradiation time for PαMeS and PpiPrαMeS. One notes that the latter polymer degrades better than the former.

In Table 7 are presented data on molecular weights, viscosity, k_H, and S min^{-1} for the ultrasonic solution degradation of PpClS ($\overline{M}_w = 1.8 \times 10^6$) at 27°C. $\overline{M}_w$ and $\overline{M}_n$, both decrease with irradiation time. S min^{-1} values of 25.0 to 268.0 $\times 10^{-3}$ from the overall $(\overline{M}_n)_0$ and $(\overline{M}_n)_t$ of PpClS are higher than those for PS which ranged between 14.0 and 44.0 $\times 10^{-3}$. S' min^{-1} calculated from the normalized GPC

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TABLE 7. Ultrasonic (70 W, 20 kHz) Solution (2% THF) Degradation of PpCIS ($\overline{M}_w$ = 1.8 × 10^6) at 27 °C for Various Periods of Time

No.	Irradiation time (min)	$\overline{M}_w \times 10^{-3}$ (GPC)	$\overline{M}_n \times 10^{-3}$ (GPC)	$\overline{M}_w/\overline{M}_n$	$[\eta]^a$ in toluene at 20° C (dL/g)	$[\eta]^a$ in THF at 25° C (dL/g)	S min^{-1} × 10^3
-	Nonirradiated	1800	1250	1.4	0.98	2.42	-
X-88	7.5	955	415	2.3	-	-	268.0
X-89	15	895	385	2.3	-	-	150.0
X-90	30	790	340	2.3	-	-	89.0
X-91	60	500	230	2.1	0.68	-	74.0
X-92	120	395	175	2.2	0.61	-	51.0
X-93	180	280	185	1.5	-	0.72	32.0
X-94	360	220	115	1.9	-	0.69	27.0
X-95	480	165	105	1.5	-	0.58	22.7

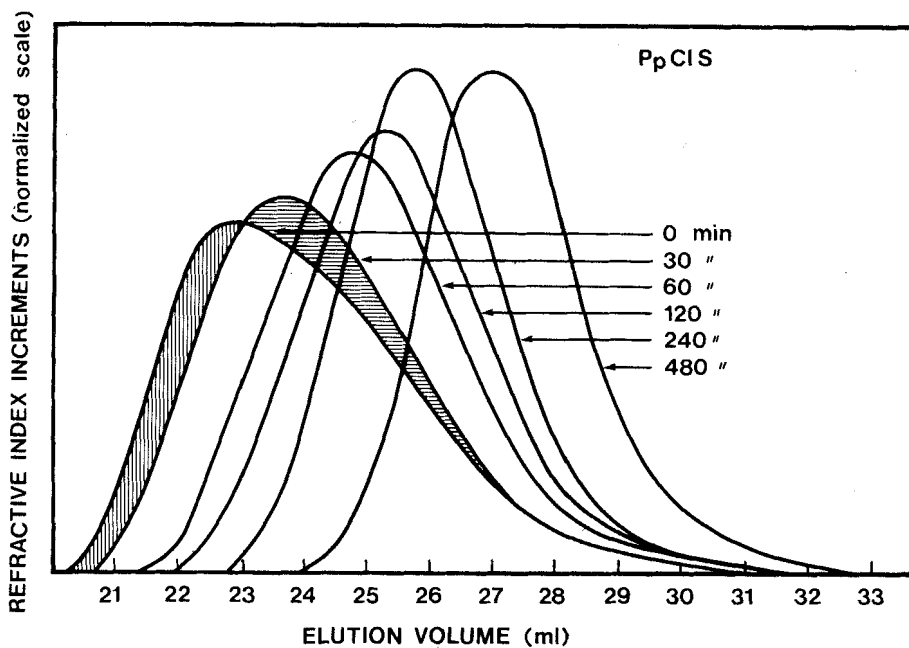^{a}Huggins coefficient for all samples of PpCIS fall between 0.33 and 0.51.

FIG. 9. Normalized GPC chromatograms before and after ultrasonic solution degradation of PpClS at 27°C for various periods of time. (See Table 7 for other data.)
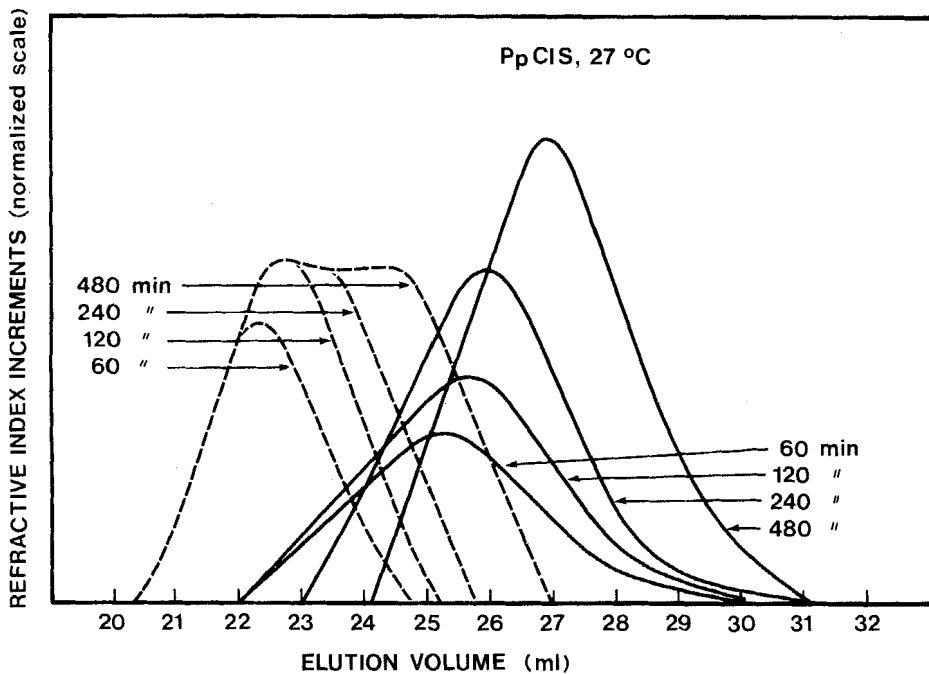
FIG. 10. Component degradation of PpClS ($\overline{M}_w = 1.8 \times 10^6$) at 27°C for various periods of time. (See Table 8 for other data.)

TABLE 8. Ultrasonic (70 W, 20 kHz) Solution (2% THF) Degradation of PpClS at 27°C for Various Periods of Time

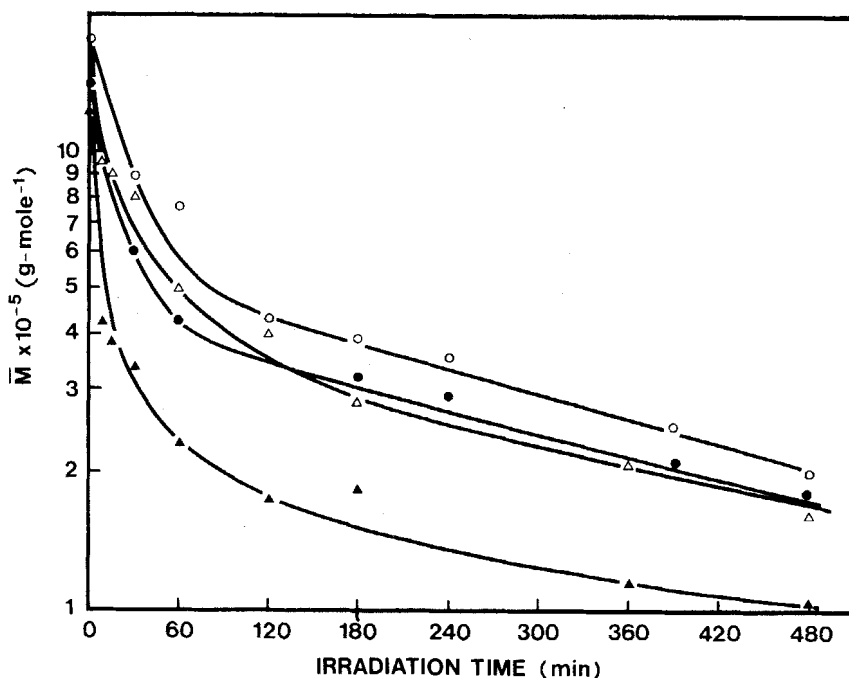| No.	Irradiation time (min)	Weight fraction (α)	Before degradation			After degradation			S' normalized values	S' min^{-1} $\times 10^3$	S min^{-1} $\times 10^3$
			$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\dfrac{\overline{M}_w}{\overline{M}_n}$	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\dfrac{\overline{M}_w}{\overline{M}_n}$			
X-91	60	0.38	163	143	1.14	45.7	27.0	1.7	1.65	27.6	74.0
X-92	120	0.56	135	114	1.19	44.6	24.1	1.85	2.15	17.9	51.0
X-93A	240	0.68	127	94.5	1.34	30.6	19.6	1.55	2.58	10.8	-
X-95	480	0.93	104	65.2	1.60	18.0	11.9	1.5	4.19	8.7	22.7

FIG. 11. Variation of $\overline{M}_w$ and $\overline{M}_n$ as a function of irradiation time for PS ($\overline{M}_w = 1.8 \times 10^6$) [42] and PpClS at 27°C. (See Table 7 for other data.) ($\circ$) PS, $\overline{M}_w$; ($\bullet$) PS, $\overline{M}_n$; ($\triangle$) PpClS, $\overline{M}_w$; and ($\blacktriangle$) PpClS, $\overline{M}_n$.

distribution comparisons (Fig. 9) leading to component tracing (Fig. 10) and their analyses (Table 8) for PpClS are lower than those of PS ($\overline{M}_w = 1.8 \times 10^6$) [42]. Higher S min^{-1} values are also evidenced by the variation of overall $\overline{M}_w$ and $\overline{M}_n$ of PS and PpClS as a function of irradiation (Fig. 11) where the latter polymer degrades faster than the former.

In Table 9 data are presented on molecular weights, viscosity, k_H, and S min^{-1} for the solution degradation of PpBrS ($\overline{M}_w = 5.6 \times 10^5$) at 27°C. $\overline{M}_w$ and $\overline{M}_n$ both decrease with irradiation time. The $\overline{M}_w/\overline{M}_n$ ratio remains constant within ±0.1 of 1.4. S min^{-1} values vary from 2.4 to 6.4 $\times 10^{-3}$ and are lower than those for PS ($\overline{M}_w = 9.0 \times 10^5$).

S' min^{-1} calculated from the normalized GPC distribution comparisons (Fig. 12) leading to component tracing (Fig. 13) and their analyses (Table 10) for PpBrS ranged between 4.3 and 7.2 $\times 10^3$ and are of the

TABLE 9. Ultrasonic (70 W, 20 kHz) Solution (2% THF) Degradation of PpBrS ($\overline{M}_w = 5.6 \times 10^5$) at 27°C for Various Periods of Time

No.	Irradiation time (min)	$\overline{M}_w \times 10^{-3}$ (GPC)	$\overline{M}_n \times 10^{-3}$ (GPC)	$\overline{M}_w/\overline{M}_n$	$[\eta]^a$ in toluene at 20°C (dL/g)	$[\eta]^a$ in THF at 25°C (dL/g)	$S \min^{-1} \times 10^3$
–	Nonirradi- ated	560	385	1.45	0.58	1.62	–
X-193	60	510	335	1.5	–	0.81	2.5
X-194	120	315	220	1.45	0.32	0.64	6.2
X-195	180	305	210	1.45	0.25	0.54	4.6
X-196	240	270	180	1.5	–	–	4.7
X-197	360	250	195	1.3	–	0.47	2.7
X-198	480	220	160	1.4	0.20	0.40	2.9

^{a}Huggins coefficient k_H from viscosity data for all samples of PpBrS fall between 0.40 to 0.68.
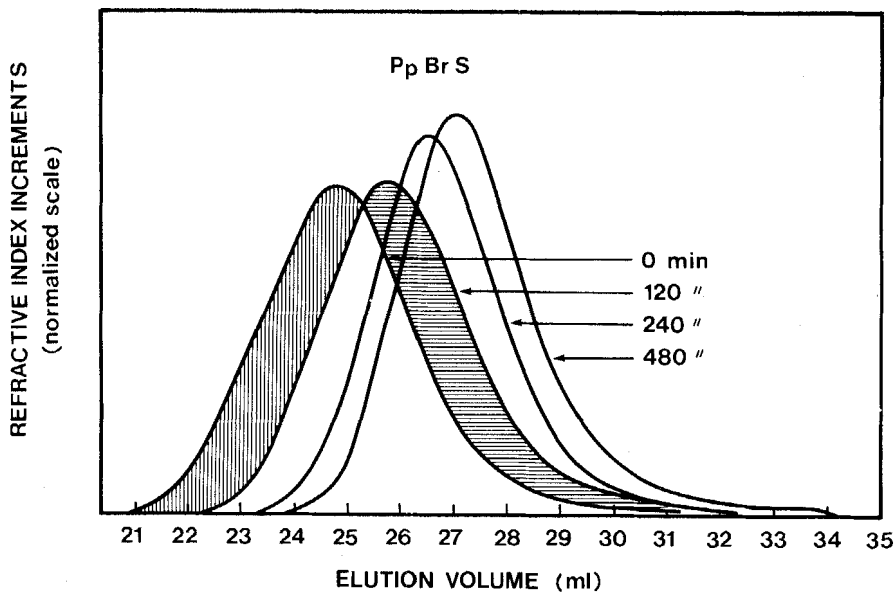
FIG. 12. Normalized GPC chromatograms before and after ultra-sonic solution degradation of PpBrS at 27°C for various periods of time. (See Table 9 for other data.)
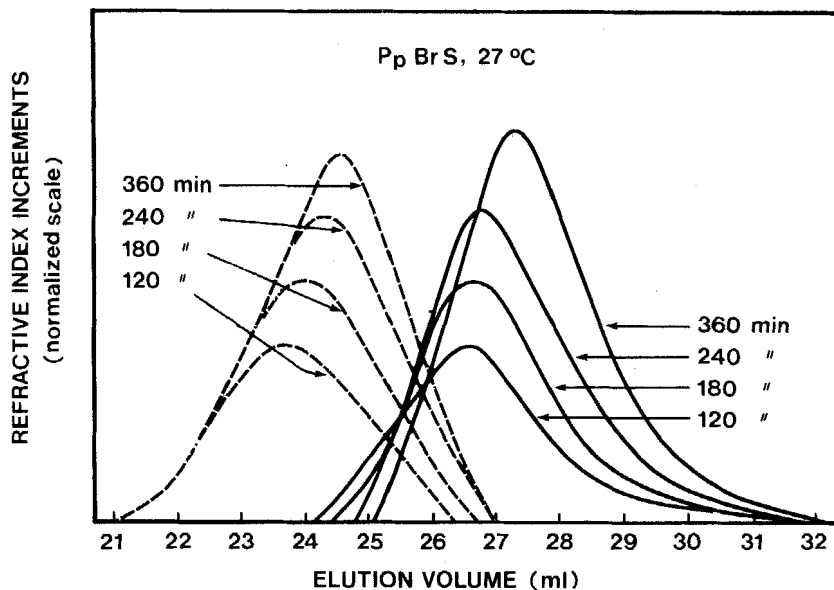

FIG. 13. Component degradation of PpBrS ($\overline{M}_w$ = 5.6 × 10^5) at 27°C for various periods of time. (See Table 10 for other data.)

TABLE 10. Ultrasonic Solution (2% THF) Degradation of PpBrS at 27°C

No.	Irradiation time (min)	Weight fraction (α)	Before degradation			After degradation			S' normalized values	S' min^{-1} $\times 10^3$	S min^{-1} $\times 10^3$
			$\bar{M}_w$ $\times 10^{-4}$	$\bar{M}_n$ $\times 10^{-4}$	$\dfrac{\bar{M}_w}{\bar{M}_n}$	$\bar{M}_w$ $\times 10^{-4}$	$\bar{M}_n$ $\times 10^{-4}$	$\dfrac{\bar{M}_w}{\bar{M}_n}$			
X-193	60	0.065	116.5	109.0	1.07	25.0	20.0	1.25	0.26	4.33	2.5
X-194	120	0.36	80.8	70.2	1.15	26.6	20.5	1.30	0.86	7.20	6.2
X-195	180	0.50	74.8	64.3	1.15	24.4	19.1	1.28	1.18	6.55	4.6
X-196	240	0.63	69.2	59.0	1.15	22.8	18.5	1.25	1.39	5.77	4.7
X-197	360	0.69	67.6	57.8	1.17	21.0	17.7	1.20	1.55	4.30	2.7
X-198	480	0.72	67.0	57.1	1.17	20.0	15.8	1.27	1.87	3.50	2.9

TABLE 11. Ultrasonic (70 W, 20 kHz) Solution (2% THF) Degradation of PpOMeS ($\overline{M}_w = 7.0 \times 10^5$) at 27°C for Various Periods of Time

No.	Irradiation time (min)	$\overline{M}_w \times 10^{-3}$ (GPC)	$\overline{M}_n \times 10^{-3}$ (GPC)	$\overline{M}_w/\overline{M}_n$	$[\eta]^a$ in toluene at 20°C (dL/g)	$[\eta]^a$ in THF at 25°C (dL/g)
-	Nonirradiated	700	40	17.5	0.82	0.86
X-80	7.5	620	34	18.2	-	-
X-81	15	570	38	14.9	-	-
X-82	30	520	42	12.4	-	-
X-83	60	430	33	13.0	-	-
X-84	120	370	35	10.5	-	-
X-85A	240	300	30	10.0	0.46	0.38
X-86	360	235	40	5.9	-	0.37
X-87	480	195	35	5.7	-	0.33

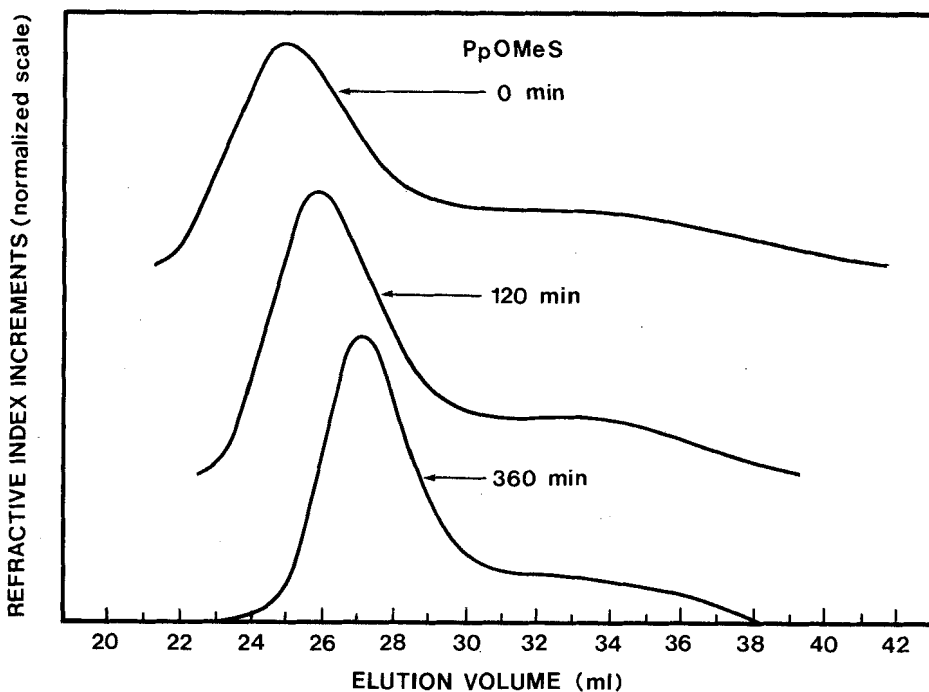[a]Huggins coefficient k_H for all samples of PpOMeS fall between 0.3 and 0.58.

FIG. 14. Normalized GPC chromatograms before and after ultra-sonic degradation of PpOMeS ($\overline{M}_w = 7.0 \times 10^5$) at 27°C for various periods of time. (See Table 11 for other data.)

same magnitude as those for PS ($\overline{M}_w = 9.0 \times 10^5$). S' min^{-1} values for PpBrS are higher than those of S min^{-1}.

In Table 11 are presented data on molecular weights, viscosity, and k_H for the ultrasonic solution degradation of PpOMeS ($\overline{M}_w = 7.0 \times 10^5$) at 27°C. $\overline{M}_w$ decreases regularly while $\overline{M}_n$ stays practically constant with increasing irradiation time. S' min^{-1} calculated from the normalized GPC distribution comparisons (Fig. 14) leading to component tracing (Fig. 15) and their analyses (Table 12) varied between 3.14 and 9.4×10^3 and are lower than those for PpBrS. These are also lower than those for PS ($\overline{M}_w = 9.0 \times 10^5$). Variation of $\overline{M}_w$ as a function of irradiation time (Fig. 16) for PpBrS and PpOMeS follows similar trends.

In Fig. 17 are shown the S' values as a function of irradiation time for the six polymers studied. These follow the order PS > PpClS > PpiPrαMeS > PpBrS > PpOMeS > PαMeS.
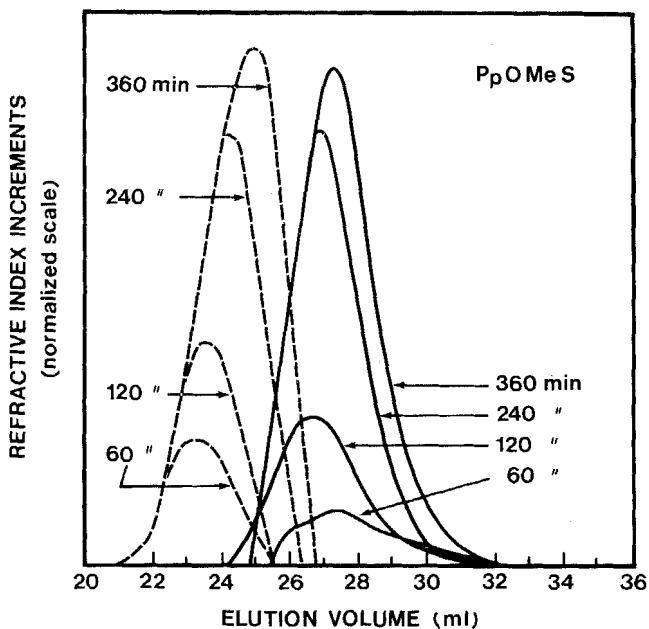
FIG. 15. Component degradation of PpOMeS at 27 °C for various periods of time. (See Table 12 for other data.)
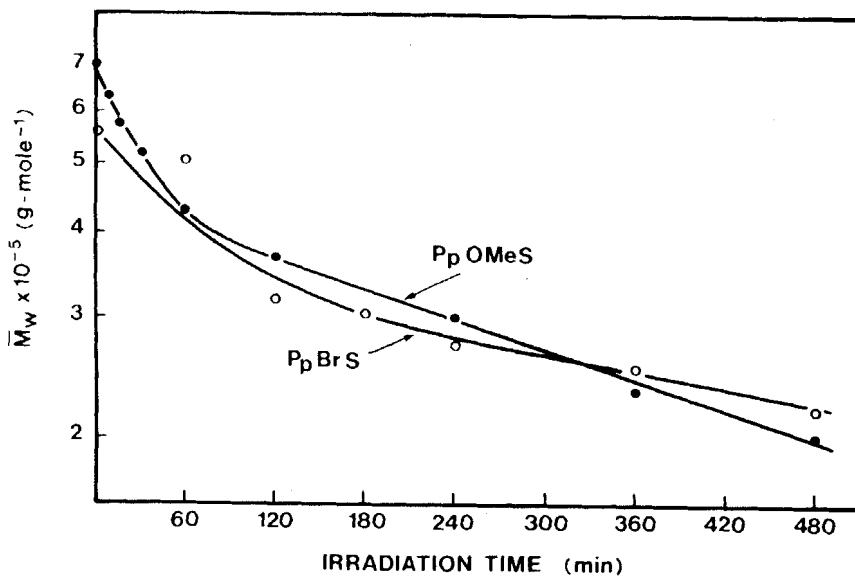

FIG. 16. Variation of $\overline{M}_w$ as a function of irradiation time for PpOMeS and PpBrS at 27°C. (See Table 7 for other data.)

TABLE 12. Ultrasonic Solution Degradation of PpOMeS at 27°C

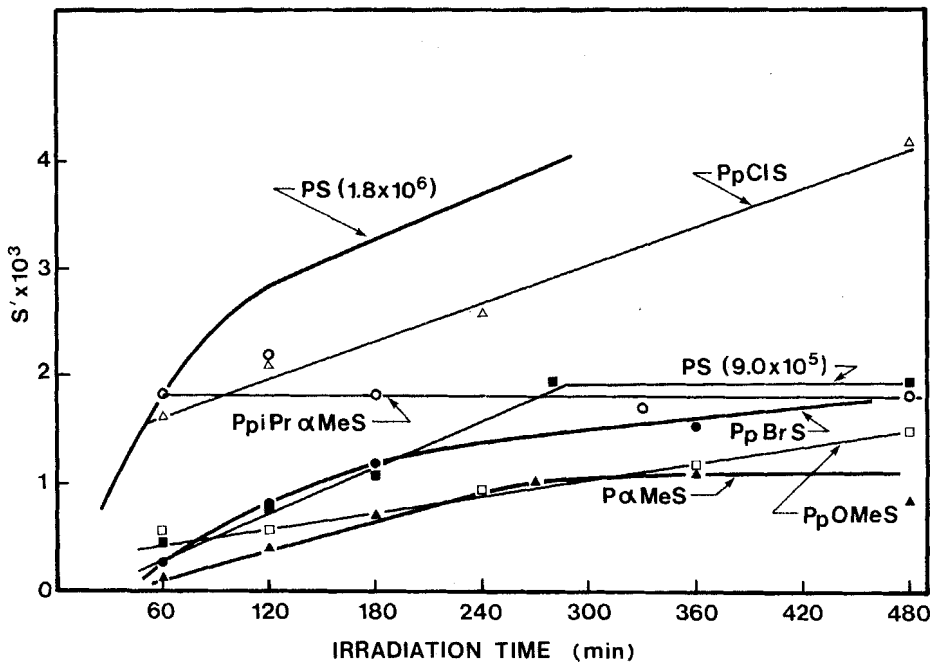| No.	Irradiation time (min)	Weight fraction (α)	Before degradation			After degradation			S' normalized values	S' min^{-1} $\times 10^3$
			$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\dfrac{\bar{M}_w}{\bar{M}_n}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\dfrac{\bar{M}_w}{\bar{M}_n}$		
X-83	60	0.08	165.0	143.0	1.15	24.4	17.8	1.37	0.56	9.40
X-84	120	0.14	151.0	132.0	1.15	34.6	25.9	1.34	0.57	4.80
X-85A	240	0.30	120.0	99.7	1.20	29.3	24.0	1.22	0.95	3.90
X-86	360	0.41	102.0	81.0	1.26	27.9	21.0	1.33	1.17	3.25
X-87	480	0.49	97.0	75.8	1.28	24.3	18.6	1.31	1.51	3.14

FIG. 17. Average number of chain scissions, S' min^{-1}, computed from the component degradation data for PS, PαMeS, PpiPrαMeS, PpClS, PpBrS, and PpOMeS as a function of irradiation time.

CONCLUSIONS

1. In the ultrasonic solution degradation of PS at 27°C, branching is not involved and a further lowering of irradiation temperature results in higher S min^{-1}. S' min^{-1} calculated from component degradation of PS is lower than that of S min^{-1}. This suggests that data on S min^{-1} cited in the literature should be treated with caution.

2. In polystyrene and substituted polystyrene solution degradations at 27°C, the average number of chain scissions per minute (S' min^{-1}) follows the order PS > PpClS > PpBrS > PpOMeS.

3. In the solution degradation of PαMeS and PpiPrαMeS of similar $\overline{M}_w$, the latter polymer has higher S' min^{-1} values. These do not result from the p-substituent isopropyl group in PpiPrαMeS but may be ascribed to the presence of a greater proportion of higher molecular weight species in PpiPrαMeS ($\overline{M}_w/\overline{M}_n = 6.0$) as compared to those in PαMeS ($\overline{M}_w/\overline{M}_n = 3.37$).

Studies are in progress on the ultrasonic solution degradations of poly(alkyl methacrylates) at different temperatures to better understand the role of substituents and temperature in shear degradations.

ACKNOWLEDGMENT

REFERENCES

[1] A. Casale and R. S. Porter, Polymer Stress Reactions, Vols. 1 and 2, Academic, New York, 1978.

[2] S. Kawase, H. Doi, and T. Kakurai, Kobunshi Ronbunshu, 35, 109 (1978).

[3] A. Henglein, Z. Naturforsch., 10b, 616 (1955).

[4] W. F. Head and W. M. Lauter, J. Am. Pharm. Assoc., 46, 617 (1957).

[5] M. A. K. Mostafa, J. Polym. Sci., 33, 295 (1958).

[6] Z. Osawa, T. Kimura, Y. Ogiwara, and M. Matsubayashi, J. Polym. Sci., A-1, 9, 2039 (1971).

[7] K. F. O'Driscoll and A. U. Sridharan, J. Polym. Sci., Polym. Chem. Ed., 11, 1111 (1973).

[8] Lord Rayleigh, The Theory of Sound, 1st. Am. Ed., Vols. 1 and 2, Dover, New York, 1945.

[9] M. Kosino and I. Miyagawa, J. Chem. Soc., Jpn. Ind. Chem. Sect., 54, 193 (1951).

[10] P. Alexander and M. Fox, J. Polym. Sci., 12, 533 (1954).

[11] H. W. W. Brett and H. H. G. Jellinek, Ibid., 13, 441 (1954).

[12] B. B. Thomas and W. J. Alexander, Ibid., 25, 285 (1957).

[13] H. U. Borgstedt, Br. J. Appl. Phys., 15, 773 (1964).

[14] D. Ensminger, Ultrasonics: The Low and High Intensity Applications, Dekker, New York, 1973.

[15] H. H. W. Brett and H. H. G. Jellinek, J. Polym. Sci., 21, 535 (1956).

[16] S. Ono, Rev. Phys. Chem. Jpn., 14, 25 (1940).

[17] S. L. Malhotra, J. Macromol. Sci.–Chem., A17, 601 (1982).

[18] M. A. K. Mostafa, J. Polym. Sci., 33, 311 (1958).

[19] R. O. Prud'homme and P. Graber, J. Chim. Phys., 46, 323 (1949).

[20] R. O. Prud'homme and P. Graber, Ibid., 46, 667 (1949).

[21] R. O. Prud'homme, Ibid., 47, 795 (1950).

[22] A. Weissler, J. Appl. Phys., 21, 171 (1950).

[23] A. Weissler, H. W. Cooper, and S. Snyder, J. Am. Chem. Soc., 72, 1769 (1950).

[24] H. W. Melville and A. J. R. Murray, Trans. Faraday Soc., 46, 996 (1950).
[25] M. A. K. Mostafa, J. Polym. Sci., 33, 295 (1958).
[26] T. Hirose, Technol. Rep. Osaka Univ., 10, 395 (1960).
[27] M. A. K. Mostafa, J. Polym. Sci., 28, 519 (1958).
[28] B. S. El'tsefon and A. A. Berlin, Vysokomol. Soedin., 4, 1033 (1962).
[29] B. S. El'tsefon and A. A. Berlin, Vysokomol. Soedin., 6, 199 (1964).
[30] B. S. El'tsefon and A. A. Berlin, Polym. Sci. USSR, 5, 668 (1964).
[31] J. Leonard and S. L. Malhotra, J. Polym. Sci., A-1, 9, 1983 (1971).
[32] J. Leonard and S. L. Malhotra, J. Macromol. Sci.–Chem., A11, 2087 (1977).
[33] S. L. Malhotra and J. M. Gauthier, Ibid., A18, 783 (1982).
[34] J. Brandrup and E. H. Immergut, Polymer Handbook, 2nd ed., Wiley, New York, 1974.
[35] Waters Associates, Gel Permeation Chromatograph Instruction Manual, Bull. No. 2, 1966, p. 2064.
[36] A. R. Shultz and S. M. Leahy, J. Appl. Polym. Sci., 5, 64 (1961).
[37] G. H. Hartley and J. E. Guillet, Macromolecules, 1, 165 (1968).
[38] J. H. Adams, J. Polym. Sci., A-1, 8, 1077 (1970).
[39] J. H. Adams, Ibid., 8, 1279 (1970).
[40] C. H. Bamford and C. F. H. Tipper, Degradation of Polymer, Elsevier, New York, 1975, p. 473.
[41] S. L. Malhotra, J. Hesse, and L. P. Blanchard, Polymer, 16, 81 (1975).
[42] S. L. Malhotra, J. Macromol. Sci.–Chem., A18, 1055 (1982).